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Governor

ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY



Misael Cabrera
Director

via e-mail

September 12, 2017
FPU18-045

Ms. Catherine Jerrard
AFCEC/CIBW
706 Hangar Road
Rome, NY 13441

RE: WAFB – ADEQ evaluation – *Review of Praxis Environmental Technologies, Inc. memorandum dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Former Williams Air Force Base, Mesa, Arizona.* Prepared for US EPA, San Francisco, CA, and ADEQ, Phoenix, AZ; prepared by AFCEC/CIBW, Dept. of the Air Force, Rome, NY; dated August 16, 2017.

Dear Ms. Jerrard:

Arizona Department of Environmental Quality (ADEQ) Federal Projects Unit (FPU) appreciates the opportunity to submit our evaluation of the AMEC-reviewed, Praxis Environmental Technologies, Inc., Time Of Remediation (TOR) memorandum. ADEQ understands that Amec Foster Wheeler (Amec) submitted the review to the Department of the Air Force, Air Force Civil Engineer Center (USAF AFCEC). Praxis Environmental Technologies, Inc., (Praxis) of Burlingame, CA, evaluated the Amec review and generated the following evaluation.

The following information sources are associated by direct reference or inference:

- Department of the Air Force, Air Force Civil Engineer Center (AFCEC) correspondence, dated August 16, 2017; sent to US EPA, San Francisco, CA, and ADEQ, Phoenix, AZ; sent by AFCEC/CIBW, Rome NY;

Subject: Submission of *Review of Praxis Environmental Technologies, Inc. memorandum dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Former Williams Air Force Base, Mesa, Arizona.*

With attached:

Review of Praxis Environmental Technologies, Inc. Dated 22 May 2017, Time of Remediation Estimates, Enhanced Bioremediation at ST012, Site ST012, Former Williams Air Force Base, Mesa, Arizona; prepared by Amec Foster Wheeler (Amec), Phoenix, AZ, dated August 2017

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- EPA and ADEQ joint correspondence; dated May 30, 2017; sent to Ms. Catherine Jerrard, AFCEC/CIBW, Rome, NY; sent by Carolyn d'Almeida, EPA Remedial Project Manager and Wayne Miller, ADEQ Remedial Project Manager.

Subject: Biodegradation Model for Enhanced Bioremediation to Address Remaining Contamination at Williams ST12 Fuel Spill Site, Mesa AZ

With attached:

Time of Remediation Estimates, Enhanced Bioremediation; prepared by Lloyd "Bo" Stewart, Praxis Environmental Technologies, Inc. (Praxis), Burlingame, CA; dated May 22, 2017

This document format provides for an overall general evaluation (Part I) performed by Praxis. Part II is a Praxis specific item evaluation.

PART I – Praxis Overall General Evaluation of Amec Review

The use of a non-equilibrium model and the instances of conservative inputs to the TOR estimates described by Amec Foster Wheeler (Amec) were not shown to be conservative in Amec's evaluation. This statement is supported by the detailed responses included in this document.

Amec states the screening model "*does not consider biological-enhancement of NAPL* [non-aqueous phase liquid] *dissolution*"; however, the screening model in the memo clearly includes biological enhancement of NAPL dissolution. The model specifically includes degradation within NAPL-impacted soils lowering the average groundwater contaminant concentration, increasing the concentration gradient between NAPL and groundwater, and thereby increasing the NAPL dissolution rate. The memo results agree with the findings of Amec-cited references on enhanced dissolution (Amos et al., 2008; Cope & Hughes, 2001). The evaluation cites two highly theoretical, academic studies that indicate the bulk mass transfer coefficient can be increased by chemical reactions if these reactions occur within a representative elemental volume (i.e., length scale on the order of numerous grain sizes) with NAPL. As described in the detailed responses, these hypothetical results have no appreciable relation to the full-scale setting at ST012.

Amec states "*the use of the non-equilibrium (NE) condition using data from the non-reactive MTT* [mass transfer test] *is inappropriate for the screening of EBR* [enhanced bioremediation] *as supported by several studies*". The cited studies have been reviewed in the responses below and are shown not to be applicable to conditions at ST012 primarily because of site heterogeneity and the scale of measurement. The cited references rely on laboratory data using a uniform sand pack. Mobile et al. (2016) provide a review of this issue as follows, "Previous studies have compared the local equilibrium and rate-limited approaches using pre-loaded, soil-packed columns (Borden and Pivoni, 1992; Seagren and Moore, 2003; Grant and Gerhard, 2007) or numerical modeling (Mayer and Miller, 1996). While these studies suggest that the local equilibrium model can perform well under certain circumstances, the results generally suggest that the rate limited approach is most appropriate at larger scales due to the potential variability in interfacial area and pore velocity (Rivett et al., 1994; Seagren et al., 1999; Grant and Gerhard, 2007; Maji and Sudicky, 2008)."

If we accept the two assumptions asserted by Amec of NAPL-water equilibrium and no appreciable dependence of mass transfer coefficients on pore velocity, TOR estimates using pump and treat can be calculated with the equilibrium equation of Section 4. In the upper water bearing zone (UWBZ) the equation indicates a TOR identical to EBR (16 years) can be achieved with an extraction rate of 67 gallons per minute

(gpm) without any biological activity. In the lower saturated zone (LSZ) the model indicates an extraction rate of only 23 gpm will yield a TOR of 12 years without biological activity.

Amec states the benzene mass transfer coefficient of 0.0042 day⁻¹ is overly conservative because the scaling methodology for assessing the benzene mass transfer coefficient described in Appendix C of the memo is questioned. The question arises because the methodology is based on pore volume exchange rates in the field and the scaling applies mass transfer correlations based on laboratory column studies. While it is agreed the Appendix C method is tenuous, it is not necessarily conservative. The tenuous nature is more dependent upon the hydrogeological heterogeneity and non-uniform NAPL distribution than absolute pore velocity.

The cited laboratory studies are only applicable to the specific scenario of NAPL pool dissolution in a uniform soil and on a length scale orders of magnitude less than ST012. Therefore the cited absolute velocities do not have applicability to the variable NAPL saturation and NAPL architecture within the field-scale heterogeneous soil volume at ST012. A detailed analysis of the bulk mass transfer coefficient based on the mass transfer test in the LSZ at ST012 is provided in Appendix H of Kavanaugh et al. (2011) concluding, "The bulk mass transfer coefficients determined from the field data are roughly three orders of magnitude less than the values calculated from literature correlations based on flow through a uniformly distributed residual NAPL. As before, this large difference was not unexpected because of subsurface heterogeneities."

Amec states the single model application of uniformly distributed 8,000 mg/L sulfate is overly conservative; however, time restraints limited the reporting of modeling results for the fate of injected sulfate and growth of SRB. Over time, the utilization of sulfate becomes limited by the mass of SRB and this biomass is limited by mass transfer of substrate from NAPL. Although not reported, modeling of additional introductions of sulfate over the ambient supply decreased the TOR only marginally as the availability of substrate became the dominant parameter and the natural supply of sulfate was sufficient. For these reasons, the assumption is not overly conservative.

Amec states that a higher total porosity is overly conservative and results in an increased TOR when the opposite occurs. Increased pore space increases the volume for biological degradation to occur per unit volume of soil with a given mass of NAPL. The total porosity can be significant in developing NAPL mass estimates as described in the detailed responses below.

Amec states an endpoint modeling concentration based on maximum contaminant levels (MCLs) for water in equilibrium with NAPL is overly conservative. However, volume averaging on the scale of the site yields exceedances of MCLs in some locations while others would be "clean" yielding an average equal to MCLs. Hence, the endpoint is reasonable and not conservative since a plan for evaluating the attainment of remedial goals has not been prepared.

Amec states first-order and Monod sulfate-biodegradation rate constants are overly conservative although no other biodegradation rate constants have been substantiated with ST012 field data. For the Monod rate constants, no justification has been provided to suggest these rates are expected to increase during EBR. The absolute hydrocarbon degradation rate is expected to increase with an increase in the mass of sulfate reducing bacteria, but the reaction rate should not be expected to change significantly.

PART II – Praxis Specific Item Evaluation of Amec Review

1. Amec Review (Background, page 1)

“Given the flux of naturally occurring soluble terminal electron acceptors (TEA) into ST012, this utilization of sulfate represents the largest fraction of petroleum-hydrocarbon biodegradation by the available TEAs. It has been estimated that sulfate reduction accounts for more than 80 percent of the naturally occurring petroleum hydrocarbon biodegradation at ST012 (BEM, 1998). Although naturally-occurring sulfate reduction of the petroleum hydrocarbon contamination is significant, it is also limited by the natural flux of sulfate supplied by upgradient groundwater.”

Praxis Evaluation

The processes of natural attenuation are occurring at ST012; the primary issue in question is the duration in time required to achieve remedial goals. Given the flux of naturally occurring sulfate flowing into ST012 and assuming complete utilization, rough estimates for current petroleum-hydrocarbon biodegradation by sulfate reduction can be calculated from zero order processes. Such calculations provide a rough scope of the impact of EBR on degradation necessary to meet remedial action objectives (RAOs) under ideal conditions. Utilizing values from Tables 1 and 8 in the subject memorandum yields the following ambient rate estimates for the UWBZ and LSZ,

$$\begin{aligned} \text{HC Degradation Rate} &= \frac{Q \bar{E}_{\text{SO}_4^{2-}}^{\text{bkgrnd}}}{\gamma_{\text{SO}_4^{2-}}} \\ \text{UWBZ HC Degradation Rate} &= \frac{(4.4 \text{ gpm}) (200 \text{ mg/L})}{4 \text{ g/g}} = 966 \text{ lbs/yr} \\ \text{LSZ HC Degradation Rate} &= \frac{(3.5 \text{ gpm}) (290 \text{ mg/L})}{4 \text{ g/g}} = 1,114 \text{ lbs/yr} \end{aligned}$$

From Table 3 of the memorandum, the initial target mass of hydrocarbon in the UWBZ is 1,650,000 lbs. (251,000 gal x 6.57 lbs./gal). To degrade 30% of this mass assuming the ambient rate (MNA) would require about 500 years. To achieve a 15 year timeframe requires an average degradation rate of about 33,000 lbs./yr. or a degradation rate increase by a factor of ~33 under ideal conditions. For the LSZ, with an estimated hydrocarbon mass of 360,200 lbs., the ambient rate yields an MNA timeframe of about 100 years (for 30% of the mass). To meet a 15-year horizon, the degradation rate must be increased by a factor of ~6.5. These simple calculations neglect other processes that will limit the rate (e.g., NAPL mass transfer); however, the magnitudes suggest the LSZ is significantly more likely to achieve a successful outcome. The theoretical results in the memorandum for the UWBZ were not suggestive of potential success in the UWBZ. Further, these estimates apply only to hydrocarbon mass found outside the former thermal treatment zone (TTZ), while the remaining mass within the TTZ after steam enhanced extraction (SEE) is unknown.

2. Amec Review (Conservative inputs that are likely not representative of EBR, page2, 1st bullet)

“Porosity values of 0.4 are overly conservative.”

Praxis Evaluation

The present author did not perform the source assessment calculations found in BEM (2011). The source assessment assumed total porosity for individual soil layers as 0.32 or 0.35 and these values were based solely on a literature review and did not consider actual site data. Groundwater modeling with MODFLOW reported

in BEM (2011) assumed an effective porosity of 0.3. Modeling of the TEE thermal processes utilized a total porosity value of 0.4 (see Appendix C, TEE Work Plan, BEM, 2007). The site geophysical data for the calculation of total porosity can be found in Table 3-1 and Table 3-2 in FFS (Amec, 2012).

The total porosity values cited in Table 3-1 of the focused feasibility study (FFS) were also calculated from measures of dry soil density and grain specific gravity (see Table 3-3 of the 1994 remedial investigation/feasibility study [RI/FS]). The average total porosities in the different zones are cobble zone (CZ) of 0.27 (n=7), UWBZ of 0.31 (n=4), LPZ of 0.37 (n=4), and LSZ of 0.40 (n=1). Hence the site total porosities do not support an overall total porosity of 0.3.

Standard calculations for porosity performed using the measured bulk density and the measured grain specific gravity in FFS Table 3-2 are provided below. The calculated porosity values are not supportive of an average total porosity of 0.3.

| Sample | Depth (ft. bgs) | USCS | Percent Moisture | Bulk Density (lb./ft3) | Specific Gravity | Porosity | Saturation |
|-----------|--------------------|-------|---------------------|---------------------------|---------------------|--------------|------------|
| SV-1-80 | 80 | SM | 4 | NT | 2.639 | | |
| SV-1-100 | 100 | GC | 16.1 | 102.3 | 2.62 | 0.375 | 0.708 |
| SV-1-120 | 120 | CL-ML | 13.1 | 101.9 | 2.639 | 0.382 | 0.563 |
| SV-1-150 | 150 | SC | NT | NT | 2.619 | NT | NT |
| SV-1-165 | 165 | CL | NT | NT | 2.653 | NT | NT |
| | | | | | | | |
| UWB-1-90 | 90 | CL | 13.7 | 108.1 | 2.642 | 0.345 | 0.692 |
| UWB-110 | 110 | CL | 9 | 109 | 2.673 | 0.347 | 0.455 |
| UWB-1-150 | 150 | CL | 18.4 | 83.3 | 2.66 | 0.498 | 0.495 |
| UWB-1-180 | 180 | SC-SM | 10 | 94.8 | 2.641 | 0.425 | 0.359 |
| UWB-1-200 | 200 | CL | 18.3 | 100.7 | 2.691 | 0.401 | 0.740 |
| | | | | | | | |
| LSZ-1-76 | 76 | CL-ML | 9.6 | 132.5 | NT | NT | NT |
| LSZ-1-136 | 136 | SC | 22.9 | 116.6 | 2.67 | 0.301 | 1.430 |
| LSZ-1-166 | 166 | CL | 31.6 | 94.9 | 2.646 | 0.426 | 1.134 |
| LSZ-1-206 | 206 | CL | 23.2 | 95.8 | 2.672 | 0.426 | 0.840 |
| LSZ-1-242 | 242 | SM | 12.6 | 94.9 | 2.628 | 0.422 | 0.456 |
| | | | | | | | |
| UWB-2-130 | 130 | CL-ML | 15.8 | 90.8 | 2.663 | 0.454 | 0.509 |
| UWB-2-150 | 150 | SC | NT | 98.6 | 2.642 | 0.402 | NT |
| UWB-2-160 | 160 | CL | NT | NT | 2.673 | NT | NT |
| UWB-2-170 | 170 | CL | NT | NT | 2.655 | NT | NT |
| UWB-2-200 | 200 | SC-SM | 19.9 | 95.5 | 2.614 | 0.415 | 0.737 |
| | | | | | | | |
| LSZ-2-196 | 196 | SC-SM | 12.8 | NT | 2.685 | NT | NT |
| LSZ-2-216 | 216 | SC | 13.5 | 115.5 | 2.616 | 0.293 | 0.857 |
| LSZ-2-226 | 226 | SM | 8.3 | 122.9 | 2.692 | 0.269 | 0.611 |
| LSZ-2-236 | 236 | SW-SM | NT | NT | 2.625 | NT | NT |

3. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 2nd bullet)

"Endpoint modeling concentration of groundwater in direct contact with light non- aqueous phase liquid."

Praxis Evaluation

The modeling in the memorandum is based on an average over the volume of NAPL-impacted soil; hence, the endpoint groundwater concentration is also an average over the source soil volume considered. Therefore, by averaging, exceedances of MCL would occur in some locations while others would be "clean" to yield an average equal to MCL. For this reason, the endpoint in the modeling is appropriate. The most stringent goal would be below MCL at all locations throughout the source soil volume. The details of the performance monitoring to assess ST012 cleanup have yet to be determined (monitoring wells, sampling methods, statistical analyses, etc.).

4. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 3rd bullet)

"Biodegradation of the solid- and liquid-phase hydrocarbons is zero. Only dissolved-phase petroleum hydrocarbon contamination is bioavailable."

Praxis Evaluation

No basis has been provided that biodegradation of solid- and liquid-phase hydrocarbons will be appreciable. The memo assumption is not overly conservative until solid- and liquid-phase hydrocarbon biodegradation proof is presented.

5. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 4th bullet)

"Rate-limited or non-equilibrium NAPL mass transfer from the liquid-to dissolved-phase under EBR does not consider biological-enhancement of NAPL dissolution."

Praxis Evaluation

As described in Section 5 and Appendix B of the memorandum, the model clearly considers biological enhancement of NAPL dissolution in contradiction to the above statement. The model specifically includes degradation within NAPL-impacted soils. In the model, degradation lowers the groundwater contaminant concentration, increases the concentration gradient between NAPL and groundwater, and thereby increases the NAPL dissolution rate. The comment appears to confuse the difference between NAPL dissolution and its dependence on the NAPL mass transfer coefficient or is referring to a hypothetical enhancement to the coefficient. Screening level models exist to calculate the fate of a downgradient dissolved plume (e.g., BIOSCREEN) but the concentration from the source is generally assumed to be at equilibrium with the NAPL and source lifespan is calculated with ad hoc methods unrelated to specific technologies. A purpose of the model is to incorporate the biological enhancement of NAPL dissolution within the source zone.

6. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 5th bullet)

"First-order and Monod sulfate-biodegradation rate constants are overly conservative as they represent the low end of natural (unenhanced) conditions. These should not be used in the context of EBR expectations."

Praxis Evaluation

No other biodegradation rate constants have been substantiated with ST012 field data or in literature. For the Monod rate constants, no justification has been provided to suggest these rates are expected to increase during EBR. The absolute hydrocarbon degradation rate is expected to increase with an increase in the mass of sulfate reducing bacteria (SRB) but the reaction rate should not be expected to change significantly. Similarly, the first-order rate constant would be expected to increase in proportion to the mass of SRB without a significant change in the reaction rates. Hence, the assumed rates are consistent with EBR expectations.

7. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 6th bullet)

"The scaling approach provided in Appendix C of the memo, and used to arrive at a benzene mass transfer coefficient of 0.0042 day⁻¹ is overly conservative as a mass transfer coefficient representative of natural or ambient biodegradation. The scaling approach considers a correlation between the mass transfer coefficient and the Sherwood Number, which is one of approximately 10 dimensional variables used to define inter-phase mass transfer rate from a LNAPL to mobile aqueous phase. The version of the Sherwood-Number/mass-transfer coefficient correlation applied to the scaling approach was arrived at through analysis of data from column studies conducted at flow rates between about 3 and 15 meters per day (m/d). While the interstitial velocities generated during the on-site mass transfer test (MTT) (Mobile et al, 2016) approach the column-study velocities, the ambient velocity is far below those during the MTT or the column studies and the correlation is likely not applicable for scaling."

Praxis Evaluation

It is agreed that the methodology for assessing the benzene mass transfer coefficient is tenuous; however, the tenuous nature is more dependent upon the site heterogeneity and non-uniform NAPL distribution than the velocity. Comparing linear flow through uniform NAPL saturations in column studies to complex three-dimensional flow through widely varying NAPL saturation and architecture is suspect. A much more detailed analysis of the bulk mass transfer coefficient in the LSZ at ST012 is provided in Appendix H of Kavanaugh et al. (2011) where it is reported (p. H-14), "The bulk mass transfer coefficients determined from the field data are roughly three orders of magnitude less than the values calculated from literature correlations based on flow through a uniformly distributed residual NAPL. As before, this large difference was not unexpected because of subsurface heterogeneities. However, the average bulk mass transfer coefficients determined from the field data provide a defensible measure of this parameter for use in modeling. The average bulk mass transfer coefficients range from 0.0076 to 0.104 1/day. The values employed in the numerical modeling reported in Section 6 of this report ranged from 0.05 to 0.5 1/day and therefore may have modestly over predicted the mass dissolution rate in the source zone." Hence, the value of 0.0042 1/day for the LSZ is less than the field evaluated range of 0.0076 to 0.104 1/day. A similar assessment was not performed for the UWBZ. Further discussion is provided under Item 19.

8. Amec Review (Conservative inputs that are likely not representative of EBR, page 2, 7th bullet)

"The one-time, 8,000 mg/L application of sulfate does not acknowledge the proposed phased EBR approach which may consist of multiple rounds of injection if needed. The application of conservative assumptions with respect to mass presence combined with limiting sulfate application prolongs the TOR."

Praxis Evaluation

The one-time application of 8,000 mg/L assumed an instantaneous, well mixed distribution of sulfate. Detailed modeling results for the fate of injected sulfate and growth of SRB were not included in the memorandum (it was already long). Over time, the utilization of sulfate became limited by the mass of SRB and this mass was limited by mass transfer of substrate from NAPL. Although not reported, modeling of additional introductions of sulfate over the ambient supply decreased the TOR only marginally as the availability of substrate became the dominant parameter. For these reasons, the assumption is not overly conservative.

9. Amec Review (Paragraph beginning reference to memo Section 4 of the TOR..., page 3)

"...if LNAPL and groundwater maintain equilibrium and benzene biodegradation rates can be sustained at 0.0125 day⁻¹, then the remedial goal (RG) for benzene would be achieved in about 12 and 16 years in the LSZ and UWBZ, respectively."

Praxis Evaluation

Assuming local equilibrium (LE) between water and NAPL as described in the Amec review, identical time of remediation results can be achieved by simply using pump and treat. In the UWBZ the LE model indicates an extraction rate of 67 gpm will accomplish the cleanup in 16 years without any biological activity. In the LSZ the model indicates an extraction rate of only 23 gpm will accomplish the cleanup in 12 years without biological activity. These flows are only 15 and 7 times greater than ambient flow, respectively. As discussed extensively in the Amec review and the citations regarding the relationship between pore velocity and mass transfer coefficients, this increase in pore velocity does not negate the assumption of local equilibrium.

10. Amec Review (Paragraph beginning reference to memo Section 4 also includes..., page 3)

“As expected, longer TOR is estimated for higher total porosity values and lower biodegradation rates; and, shorter TOR is estimated for lower porosities and higher biodegradation rates.”

Praxis Evaluation

As illustrated in Figure 1 of the Amec review and Table 5 from the memo, this statement is inaccurate regarding the calculated NAPL volume scenarios. The calculated NAPL volume was based on measured soil concentrations (by mass) and therefore a higher porosity yields a lower NAPL saturation, more water saturated volume for biological degradation, and a shorter TOR.

11. Amec Review (Paragraph reference to memo Section 4, Amec review text beginning *It is likely that* ..., page 3, continuing to page 4)

“It is likely that implementing EBR will biologically enhance the dissolution of LNAPL (Chu et al, 2006). The increase in biologically enhanced LNAPL dissolution by EBR will maintain LNAPL mass transfer at rates that approach those estimated by the LE model until groundwater chemicals of concern (COCs) reach [remedial goals] RGs. This is conceptualized by the screening-level estimates described in Section 4 of the memo. Therefore, the LE model presented in Section 4 of the memo provides an appropriate screening-level evaluation of the EBR design approach. Other researchers have implemented the LE model to assess biologically enhanced LNAPL dissolution in porous media (Bahar et al, 2016)...”

[page 4] *...Researchers have measured biological enhancement of LNAPL dissolution that result in up to a 16 time increase of the abiotic mass transfer coefficient (Amos, 2008; Cope, 2001).*

Praxis Evaluation

As described in a previous statement, the screening model includes enhanced NAPL dissolution associated with degradation that increases concentration gradients in the considered field length scales. In that sense, the memo fully agrees with the findings of Amos et al. (2008) and Cope & Hughes (2001). Without biological degradation within the NAPL source soils the TOR increases in multiples consistent with the findings in those papers.

The statement, *“The increase in biologically enhanced LNAPL dissolution by EBR will maintain LNAPL mass transfer at rates that approach those estimated by the LE model until groundwater chemicals of concern (COCs) reach RGs”* is the basic assumption probed in the TOR memo.

However, the cited works by Chu et al. (2007) and Bahar et al. (2016) are purely academic, mathematical studies of idealized scenarios. Chu et al. (2007) draw broad conclusions about bulk mass transfer coefficients without describing the several underlying assumptions that can vastly narrow applicability of their assertions in a field setting. In particular, the study presumes the dominant length scale is the diffusion path length through water in the midst of a uniformly distributed NAPL in a uniform soil material. They do not acknowledge (at least not in the abstract) that such a system does not exist in nature. In field settings with

heterogeneity in both soil material and NAPL distribution, the length scales are increased (Mobile et al., 2016). In addition, the length scale associated with interphase mass transfer in a multicomponent NAPL is assumed inconsequential although this phenomenon is described in other cited references (Seagren et al., 2003; Bahar et al., 2016). With respect to the model of biological degradation, all of the results and assertions are drawn with the assumption of a simple first order decay reaction. This assumption implies a myriad of underlying mass transfer assumptions that are likely not met in a field setting of sulfate reduction. Examples include the length scale for transport of dissolved sulfate, the mass and distribution of SRB, the existence and length scale for transport of nutrients, and the potential inhibition from increased contaminant concentrations proximate to NAPL. The inhibition issue was studied in Amos et al. (2008) for tetrachloroethylene (PCE). The theoretical study of Bahar et al. (2016) included more phenomena and was intended to “provide a better insight on the impact of biofilm dynamics near NAPL sources through the upscaling process.”

12. Amec Review (Paragraph reference to memo Section 4, Amec review text beginning *EBR, primarily by the addition of...*, page 4)

“EBR, primarily by the addition of TEA, is designed to achieve/maintain equilibrium as described by the LE model. The ST012 EBR design relies on advective and dispersive transport in the active phase and diffusive transport in the immobile, inactive phases; as well as enhanced sulfate respiration that maintains NAPL-water-soil equilibrium until groundwater COCs have achieved RGs.”

Praxis Evaluation

EBR is not designed to achieve/maintain equilibrium but rather to increase the dis-equilibrium of the concentration gradient between the NAPL and water to increase the dissolution rate. Decreases in the mass transfer characteristic length scale in the field should not be expected (Mobile et al., 2016).

13. Amec Review (Paragraph reference to memo Section 5, Amec review text beginning *Section 5 presents the....*, page 4)

“The NE model is used to estimate TOR considering EBR that does not enhance NAPL dissolution dissolution, and the rate of LNAPL dissolution is restrained below equilibrium due to abiotic, site-specific limiting factors.”

Praxis Evaluation

This description of the NE model is not accurate. The NE model includes a biological enhancement to NAPL dissolution, tempered by the physical mechanisms of dissolution and is consistent with cited references (Amos et al., 2008 and Cope & Hughes, 2001).

14. Amec Review (Paragraph reference to memo Section 5, Amec review text beginning *Section 5 presents the....*, page 4)

“...the NE model TOR estimates are approximately equal to the LE model TOR estimates. Considering...2. a sustainable first-order biodegradation rate for benzene...”

Praxis Evaluation

The assumption of a simple, sustainable first-order biodegradation rate implies a myriad of underlying mass transfer assumptions that are likely not met in a field setting of sulfate reduction. Examples include the length scale for transport of dissolved sulfate, the mass and distribution of SRB, the existence and length scale for transport of nutrients, and the potential inhibition from increased contaminant concentrations proximate to NAPL.

15. Amec Review (Paragraph reference to memo Section 5, Amec review text beginning Section 5 presents the..., Paragraph after 1st numeric points, page 4)

"LNAPL dissolution and biodegradation rates that are limited only by LNAPL dissolution equilibrium are readily achievable. The increase in LNAPL dissolution anticipated by EBR will likely maintain LNAPL dissolution rates at equilibrium conditions throughout the TOR"

Praxis Evaluation

Praxis requests intent and meaning clarification. The above statements are not clear.

16. Amec Review (Paragraph reference to memo Section 5, page 5, 2nd paragraph)

"The approach to scaling of the mass transfer coefficient values from the test to current conditions considering LNAPL saturation is reasonable and acknowledges that mass transfer rates are transient and proportional to LNAPL saturation (Powers et al, 1994). Moreover, it is acknowledged [in the TOR memo] that without biological enhancement of LNAPL dissolution, the mass transfer rates of NAPL components will likely decrease with the ambient depletion of LNAPL saturations."

Praxis Evaluation

The mass transfer rates of NAPL components will eventually decrease with the depletion of LNAPL saturations and components whether biological enhancement occurs or not.

17. Amec Review (Paragraph reference to memo Section 5, page 5, 3rd paragraph)

"A major assumption in Appendix C sets the baseline of the mass transfer coefficient determined by the on-site test at 0.05 day⁻¹. This baseline value for the mass transfer coefficient is highly conservative; the mass transfer coefficients determined as a result of the on-site test were 0.6, 0.4, and 0.022 day⁻¹. Referring to the method applied to scale mass transfer coefficients (Clement et al, 2004), the maximum value of 0.6 day⁻¹, not a minimum value, is likely more appropriate for scaling."

Praxis Evaluation

The cited values are for the LSZ; estimates for the UWBZ were not generated. These values were measured on the scale of tens of feet. The site-specific modeling of ST012 utilized a mass transfer coefficient of 0.05 day⁻¹ (Kavanaugh et al., 2011) to account for the increased scale of the modeled soil volume because the bulk mass transfer coefficient is scale dependent.

18. Amec Review (Paragraph reference to memo Section 5, page 5, 4th paragraph)

"The scaling of the mass transfer coefficient values from the test to current conditions considering the pore volume exchange rate is exceedingly conservative and may not have been correctly applied. The MTT paper (Mobile et al, 2016) stated that, "...pore velocity should have negligible impact on predicted values of K_f^N ". Nevertheless, the TOR memo presents an approach to interstitial-pore-water-velocity scaling of the mass transfer coefficient..."

Praxis Evaluation

The inference of an incorrect application based on the Mobile et al. quote leaves out context. The full text is, "In the case of the ST012 MTT, the high degree of material heterogeneity combined with significant residual presence would lead to the expectation that pore velocity should have a negligible impact on predicted values of K_f^N ." In other words, the high degree of soil heterogeneity and variable NAPL saturation found at ST012 create such long diffusion path lengths for mass transfer such that changes in the pore velocity are not expected to have a significant impact on mass transfer on the scale of the mass transfer test. However, the bulk mass transfer coefficient is scale dependent and pore velocity is expected to have an influence on the

scale of the soil volumes in the screening model that are similar to those in Kavanaugh et al. (2011). For this reason the scaling is not exceedingly conservative. We are open to the use of other viable methods of scaling.

19. Amec Review (Paragraph reference to memo Section 5, page 6, portions of 1st and 2nd paragraphs)
The research [Seagren et al, 2003] concluded that the LE and NE model predictions for LNAPL dissolution converge at average pore water velocities below approximately 10 m/d. The average pore water velocities at ambient conditions and those induced during the on-site MTT test are significantly less than 10 m/d at approximately 0.02 and 0.9 m/d, respectively.

Previous research has evaluated when the LE and NE model predictions converge (Seagren et al, 1999). In this research, the convergence of the LE and NE models is dependent on the value of the product of the modified Sherwood Number and the Stanton Number, another dimensional variable used in the theoretical rationalization of the mass transfer term. This research concluded that the equilibrium boundary condition was invalid for high velocities (20 m/d), which are approximately 100 times greater than the ambient velocities at the site (0.02 m/d).

Praxis Evaluation

The Amec review implies the relatively low velocities experienced in the MTT would yield equilibrium based on the work of Seagren et al. (1999, 2003); however, that did not occur as illustrated in Figures 8 and 9 of Mobile et al. (2016). The Seagren et al. laboratory studies are only applicable to the specific scenario of NAPL pool dissolution in a uniform soil and on a completely different length scale than ST012. Therefore the cited absolute velocities do not have applicability to the variable NAPL saturation and NAPL architecture within the field-scale heterogeneous soil volume at ST012. The Seagren et al. results are dependent upon the length scale of the experiments and the formation of a boundary layer along the pool. In addition, these absolute velocities and conclusions do not account for the increasing concentration gradient and dissolution rate associated with biological degradation. The mass transfer coefficient may not change appreciably as a result of the degradation; however, threshold velocities associated with non-equilibrium would decrease as a result.

20. Amec Review (Paragraph reference to memo Section 5, page 6, portion 3rd full paragraph)
"...it is unclear if the half-saturation concentrations and the maximum utilization rates were varied or just the maximum utilization rates."

Praxis Evaluation

Only the maximum utilization rates were varied. Half-saturation concentrations were not varied and inhibition at elevated sulfate concentrations was neglected.

21. Amec Review (Conclusion, page 7, portion of 2nd bullet)
"Scenarios that combined several conservative inputs and approaches obviously result in increased TORs. However, the basis presented in the TOR memo to conclude that these scenarios are more likely to be representative than other scenarios is limited, and it is likely these scenarios represent extreme cases that are not representative of actual conditions."

Praxis Evaluation

The review concludes that "it is likely these scenarios represent extreme cases" but does not support this statement. The TOR memorandum purposely avoided drawing conclusions. The memo presented screening models of varying complexity, an array of input data, and the resulting output. Time did not permit nor did necessity require performance of a more complete sensitivity analysis.

22. Amec Review (Conclusion, page 7, portion of 4th bullet)

“...the use of the NE condition using data from the non-reactive MTT is inappropriate for the screening of EBR as supported by several studies (Amos, 2008; Bahar et al, 2016; Cope, 2001; Chu et al, 2006; and Seagren et al, 1999).”

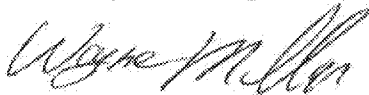
Praxis Evaluation

An extensive discussion regarding the cited references and the use of the local equilibrium and non-equilibrium are provided under Items 11 and 19. The use of non-equilibrium is justified from the results of the MTT and the less than equilibrium groundwater concentrations measured at the site within NAPL contaminated soil volumes. Mobile et al. (2016) provide a review of this issue as follows, “Previous studies have compared the local equilibrium and rate-limited approaches using pre-loaded, soil-packed columns (Borden and Piwoni, 1992; Seagren and Moore, 2003; Grant and Gerhard, 2007) or numerical modeling (Mayer and Miller, 1996). While these studies suggest that the local equilibrium model can perform well under certain circumstances, the results generally suggest that the rate limited approach is most appropriate at larger scales due to the potential variability in interfacial area and pore velocity (Rivett et al., 1994; Seagren et al., 1999; Grant and Gerhard, 2007; Maji and Sudicky, 2008).”

Closure

ADEQ may add or amend this evaluation if evidence to the contrary of our understanding is discovered; if received information is determined to be inaccurate; if any condition was unknown to ADEQ at the time this document was submitted or electronically delivered; if other parties bring valid and proven concerns to our attention; or site conditions are deemed not protective of human health and the environment within the scope of this Department.

Thank you for the opportunity to provide our evaluation. Should you have any questions regarding this correspondence, please contact me by phone at (602) 771-4121 or e-mail miller.wayne@azdeq.gov.



Sincerely,
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